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THE RHODIUM CARBONYL HYDRIDE SPECIES
A THEORETICAL AND EXPERIMENTAL INVESTIGATION

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THE RHODIUM CARBONYL HYDRIDE SPECIES. A THEORETICAL AND EXPERIMENTAL

INVESTIGATION

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ABSTRACT

A theoretical investigation (ab initio) and experimental data have been combined in an attempt to characterize the rhodium carbonyl hydride species which has been shown previously in these laboratories and in those of Solymosi to be a long-lived surface species for supported rhodium in the catalytic hydrogenation reactions for CO and CO_2. The calculations have predicted that a bent rhodium carbonyl hydride species is much more stable than a rhodium formyl species. They have also predicted that the Rh-H stretching frequency should be more than 300 cm^{-1} lower than the C-O stretching frequency for the rhodium carbonyl hydride species. This prediction is at odds with assigned Rh-H stretching frequencies for Rh organometallic complexes which place Rh-H and C-O stretching frequencies in the same region of the spectrum (2000 - 2200 cm^{-1}). The experimental data are not conclusive on this point. The calculations do satisfactorily rationalize the enhanced dissociation of the C-O bond for the rhodium carbonyl hydride species caused by the presence of the hydride moiety.

INTRODUCTION

Work in these laboratories in recent years has focused on the search for intermediates in the reactions of hydrogen with carbon monoxide[1,2] and carbon dioxide[3-5] over supported rhodium films; infrared spectroscopy has been the primary analytical probe employed in these studies. A key Rh surface species which has been identified by infrared for both of the hydrogenation reactions is the carbonyl hydride shown below which exhibits an infrared band in the

region 2020-2045 cm^{-1} dependent upon the nature of the support and whether one or two hydride surface atoms are present.[5] Solymosi and coworkers were the first to postulate the existence of the rhodium carbonyl hydride species produced during the reduction of CO_2 over supported Rh.[6,7] It has been concluded that the presence of the hydride moiety causes a shift of the frequency for the CO stretching mode to a lower value (2020-2045 cm^{-1}) than that for the "linear" Rh_x-CO species (2040-2080 cm^{-1}) due to electron donation into the π^* orbital of the CO moiety.[1-9] This satisfactorily explains the resulting weakened CO bond, leading to its facile dissociation when hydrogen is present. This argument was challenged by Iizuka and coworkers who concluded that the low frequency CO mode was not due to a carbonyl hydride species, but rather merely to the usual linear Rh-CO species at low coverage.[10,11] However, the argument of Iizuka and coworkers seemed improbable to us because the linear Rh-CO species is always accompanied by a bridged Rh_2CO species having a broad infrared band in the 1840-1920 cm^{-1} region; both species are formed on metallic cluster sites.[12] The only surface species detected by infrared for the hydrogenation of CO_2 over supported Rh is the one (carbonyl hydride) exhibiting an infrared band in the 2020-2045 cm^{-1}

region. This was borne out by deuterium experiments in these laboratories which showed conclusively (a small observed red shift) that the species producing the infrared band in the 2020-2045 cm^{-1} region was indeed a rhodium carbonyl hydride.[4] In a very recent study Solymosi and Pásztor have shown that the presence of the rhodium carbonyl hydride species during the hydrogenation of CO_2 prevents the disruption of Rh clusters such that the usual gem-dicarbonyl species always detected during CO hydrogenation on isolated Rh^{+} sites can not form.[13]

It should be noted that a formyl species might also be considered

$$H - C^{\nearrow O}_{\ \ \big|} $$
$$Rh$$
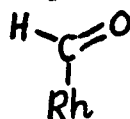
as a possible intermediate in the hydrogenation of CO and/or CO_2. However, this surface species has not been detected for supported Rh catalysts. Indeed, Yates and Cavanagh have reported a Herculean effort in which the formyl species was sought, but could not be observed.[14] One might pose the question; why is the rhodium carbonyl hydride species observed, while a rhodium formyl species is not? The purpose of the current work was to address this question using high quality ab initio computations and Fourier transform infrared spectroscopy. This work represents one of the initial attempts at using ab initio molecular orbital calculations for transition metal species relevant to surface chemistry.

THEORETICAL AND EXPERIMENTAL SECTION

For the computations in this study, the 36 core electrons of Rh were replaced by a relativistic effective core potential (RECP) as generated by Hay and Wadt.[16] The (5s4d5p) valence orbitals were represented by a (3s3p4d) primitive Gaussian basis contracted to (1s1p1d) to form a basis set denoted

4

BAS1. A basis set denoted BAS2 was formed by splitting off the outermost primitive to form a (2s2p2d) contraction. A standard 6-31G basis[17] was used for C and O in BAS1, while a set of diffuse s and p functions was added to C and O (6-31+G)[17] in BAS2. Hydrogen was described by four primitive gaussians; the inner three were contracted as found in the 6-31G basis, while the outer gaussian was varied independently with an exponent of 0.1219. The basis set BAS1 was used to calculate optimized geometries and force constants. All geometric variables were optimized[18] within the assumed symmetry point group, and frequencies were computed by taking finite differences of analytical first derivatives. The basis set BAS2 was used to determine electron populations. The "best" energies to be discussed were determined from MP3/BAS2 energies and zero point correction from vibrational frequencies (corrected by a factor of 0.89)[19] at the BAS1 level.

The experimental procedures employed in these laboratories for infrared investigations of supported Rh catalyst films have been discussed in detail.[1-5,12] Briefly, samples consisting of thin films (4.3 mg cm^{-2}) of 2.2% Rh/TiO_2 were prepared by spraying a slurry of $RhCl_3 \cdot 3H_2O$ and TiO_2 (Degussa Titanium Dioxide P25, 50 $m^2 g^{-1}$) in water/acetone from a specially designed atomizer onto a 25 mm CaF_2 infrared window held at ca. 360 K. The solvents rapidly vaporized leaving a film of $RhCl_3 \cdot 3H_2O/TiO_2$ adhered tightly to the window. The window containing the catalyst was mounted in a specially designed Pyrex infrared cell[5] which was evacuated to ca. 10^{-6} torr using an ion pump. The sample was then reduced with 85 torr doses of hydrogen gas at 480 K for periods of 5, 5, 10, and 20 min, each reduction cycle followed by evacuation. After heating for 1 h at 490 K under vacuum, the sample was evacuated overnight to ca. 10^{-6} torr at ambient temperature. Then a 77.4 torr mixture of CO_2 and H_2 at a ratio of 1:4 was added to the cell, and the

methanation reaction was initiated at 440 K for 1 h followed by evacuation to 10^{-3} torr at ambient temperature. At this point spectrum a in Figure 2 was recorded. Then 100 torr D_2 was dosed into the cell, left overnight, at ambient temperature, and spectrum b in Figure 2 was recorded. These spectra were recorded on an IBM IR/32 Fourier transform infrared spectrometer (500 scans) at 4 cm^{-1} resolution using a DTGS detector.

RESULTS

The computed optimized geometries of the various Rh species and CO and HCO are given in Figure 1. Molecular and electronic symmetries, total energies, and zero point energies for the relevant species are presented in Table I. Table II summarizes the relative energies of the various species on the HRhCO potential energy surface. It is clear that the bent form (86.6°) of the rhodium carbonyl hydride was predicted to be considerably more stable than the linear form or the rhodium formyl species. The ^2D state for Rh could not be determined at the BAS2 level because of the collapse of the wavefunction to one with extensive spin contamination. Table III presents computed bond energies for the species relative to fragments in their most stable electronic states. Table IV provides calculated vibrational frequencies and intensities for the Rh species and CO and HCO; the vibrational frequencies for RhCO could not be determined due to convergence problems.

Figure 2 shows the infrared spectra for the rhodium carbonyl hydride and rhodium carbonyl deuteride species adsorbed on a 2.2% Rh/TiO_2 catalytic film.

DISCUSSION

The _ab_ _initio_ computations for the various rhodium species reported in this work, of course, refer to gas-phase species, rather than true surface

species. Thus variation of the calculated energies, bond energies, and vibrational frequencies from the true values for the adsorbed species are to be expected. Nevertheless, it is believed that the theoretical data generated in this work can provide at least a qualitative description of the potential energy surface for the rhodium carbonyl hydride and rhodium formyl species.

Some experimental data do exist which can be compared with the ab initio predictions. Using mass spectral data, and based upon an empirical relationship between electron affinities and bond dissociation energies of diatomic metal hydrides, Squires has estimated the Rh-H bond energy to be 53.7 kcal/mol.[22] At the MP3/BAS2 + ZPC/BAS1 level of theory, which was the best level employed in this work, the Rh-H bond energy is predicted to be 73.1 kcal/mol (Table III). However, the computed ^{1}Rh-H bond energy which was 48.5 kcal/mol is in better accord with the experimental estimate. Even though ^{3}Rh-H is the ground state for gaseous Rh-H, the ^{1}Rh-H may be a more realistic model for the supported catalyst. Connor et al.[23] concluded that the strength of the Rh-CO bond in $Rh_6(CO)_{16}$ was 39.6 kcal/mol, and Somorjai et al.[24] estimated the energy of the Rh-CO bond for Rh(100) and Rh(111) single crystals (from thermal desorption studies) to be 31 and 29 kcal/mol, respectively. Table III shows that the Rh-CO bond energy was predicted to be 11.0 kcal/mol for ^{4}Rh-CO and 28.6 kcal/mol for the carbonyl hydride species at the best level of theory employed here. A recent X-ray structure determination has provided a value of 1.56 A for the Rh-H bond distances in the complex $Rh(H)_2I[NH(SiMe_2CH_2(i-Pr)_2)_2]$ which is close to the value (1.547 A) predicted by the ab initio calculations for the bent carbonyl hydride species. Typical Rh-C bond lengths[25] fall in the range of 1.78 to 2.01 A which indicates that the ab initio procedure does well at predicting Rh-CO bond lengths (see Figure 1). The absorption frequencies calculated (Table IV) for CO and HCO were

reasonable for an SCF MO method; the bending mode was particularly well reproduced for both HCO and DCO.

It is interesting that the _ab_ _initio_ calculations predict the Rh-H bond to be very strong (92.9 kcal/mol) and the Rh-H stretching mode to exhibit the most intense band in the infrared spectrum of the carbonyl hydride species. In fact, the presence of CO is predicted to enhance the strength of the Rh-H bond. Repeated attempts have been made in these laboratories and elsewhere to observe the Rh-H stretching frequency for supported Rh catalysts. If a Rh/Al_2O_3 or Rh/TiO_2 film is prepared in the manner discussed in the Theoretical and Experimental Section, and then exposed to H_2 or D_2 at pressures up to 100 Torr, with no CO or CO_2 present, no band which can be obviously attributed to Rh-H or Rh-D is observed. In fact, there is no band at all in the 1800-2200 cm^{-1} region. Yet this does not preclude the presence of CO as a stabilizing influence on a Rh hydride, and many workers have assigned bands in the 2000-2200 cm^{-1} region for organometallic rhodium hydride complexes to the Rh-H stretching mode.[26] Also, Iwasawa and Sato[27] claim to have detected a "mononuclear, rhodium-monohydride species" with an associated infrared band at 2048 cm^{-1} during the hydrogenation of $Rh(\eta^3-C_3H_5)_3/TiO_2$.

The frequencies predicted for the Rh-H and Rh-D stretching modes of the carbonyl hydride (deuteride) species led us to reexamine the infrared spectra of these species; previously only one band in the 2020-2045 cm^{-1} region had been noted and assigned to the C-O stretch for the species.[1-9] The data in Figure 2 clearly show that the band at 2037 cm^{-1} which shifts to 2032 cm^{-1} upon deuterium exchange must be assigned to a CO stretching mode, because if it were due to an Rh-H stretch, the isotopic shift would be ca. 600 cm^{-1} to lower frequency. However, a broad band is observed in spectrum b of Figure 2

at ca. 1450 cm^{-1} which is more intense than the wing of the intense 1615 cm^{-1} band in spectrum a. This could possibly be due to a shift of a weak component of the 2037 cm^{-1} band noted in spectrum a of Figure 2. In other words, the bands for the C-O and Rh-H stretching modes of the carbonyl hydride species may fortuitously overlap. However, the _ab initio_ calculations predict that the Rh-H stretching frequency should be near 1643 cm^{-1}, while the C-O stretching frequency should be at 1971 cm^{-1}. If the 66 cm^{-1} error for the C-O mode is incorported into the predicted Rh-H stretching frequency, the _ab initio_ calculations suggest that an infrared band should occur near 1709 cm^{-1}. This band may be under the wing of the intense 1615 cm^{-1} band (spectrum a) which is due primarily to the hydrated support. It is very interesting that the calculations predict an isotopic shift of only 3 cm^{-1} for the C-O stretching mode upon deuterium exchange; the observed value was 5 cm^{-1}. Further, the calculations predict that a band should exist near 1233 cm^{-1} (corrected from 1169 cm^{-1}) corresponding to the Rh-D stretching mode of the carbonyl deuteride. There was a prominent feature observed at 1193 cm^{-1} in spectrum b of Figure 2, but unfortunately O-D groups on the hydrated support would also be expected to produce a band in this region. In fact when D_2O was added to the cell, a large band peaked near 1205 cm^{-1}. In summary, it is likely that we have observed the Rh-H band, but we can not at this point be certain whether it lies under the C-O band at 2037 cm^{-1} or under the hydrated support band at 1615 cm^{-1}. Likewise, the Rh-D band must either occur at 1450 cm^{-1} or under the 1193/1205 cm^{-1} O-D support band. Of course, the solution of this dilemma, if and when it can be found, may determine the worth of the _ab initio_ procedure which was employed for use in future calculations related to surface chemistry.

Several other interesting points evolved from the _ab_ _initio_ calculations performed in this study. First, the ground state of the rhodium carbonyl hydride species (bent form) was predicted to be 28.5 kcal/mol more stable than the rhodium formyl species. There was a zero energy barrier predicted for the conversion of the formyl species to the carbonyl hydride species. These facts explain why the rhodium formyl hydride species could not be detected by Yates and Cavanagh.[14] Second, the rhodium carbonyl hydride gas-phase molecule was predicted to have a bent ground state with a HRhC bond angle of 86.6°. This is gratifying because the carbonyl hydride species on Rh/TiO_2 would be expected to be bent, and a HRhC bond angle near 90° would seem optimum. Thus, we are reasonably confident that the gas-phase _ab_ _initio_ calculations can be at least qualitatively extrapolated to the supported catalyst situation. Third, the _ab_ _initio_ calculations predict a short, stronger Rh-C bond exists for the carbonyl hydride species than for RhCO. Thus there is greater electron donation from CO toward Rh through the Rh-C σ bond for the former. Also, the carbonyl hydride species provides better overlap between Rh and the π* orbital on CO because of the short Rh-C bond. These two modes for electron transfer satisfactorily explain why the CO bond is considerably weakened when the hydride ligand is present. This is, of course, the most likely reason why the presence of H_2 in a reactor greatly enhances the dissociation of a CO bond for a rhodium carbonyl species. It explains why hydrogen is necessary to cause the dissociation of CO_2 on Rh,[5] and it probably explains the formation of active carbon on Rh in the catalytic methanation reaction. In some experimental situations the dissociation of the CO bond in the rhodium carbonyl hydride species could be the rate determining step for formation of methane and other hydrocarbons. It should be noted that we can not completely rule out the possibility of a transient formyl species being involved in the

enhanced CO dissociation in the presence of hydrogen given that the energy barrier predicted for passing from the carbonyl hydride species to the formyl species was only 28.5 kcal/mol.[28]

Carter and Goddard have recently performed GVB ab initio computations concerning the insertion of CH_2 into an adjacent Ru-H bond.[29] They found that the results were affected markedly depending upon whether electron correlation was or was not included in the calculations. At the Hartree Fock level without CI there was no energy barrier predicted for the insertion reaction, while at the GVBCI-MCSCF level an activation barrier of 11.5 kcal/mol was predicted.[29] We find also that the inclusion of electron correlation significantly affects the results for the conversion of the rhodium formyl species into the rhodium carbonyl hydride species. In fact, from Table II it is evident that the inclusion of CI caused the energy of the rhodium formyl species to increase by 10.6 kcal/mol. Also, an energy barrier was present at the HF level, but not at the MP3 level, for the interconversion between the carbonyl hydride and formyl species (see TS energies in Table II). Thus calculations at the HF level may give misleading results for insertion reactions into metal hydrogen bonds, and we recommend the inclusion of electron correlation for such reactions.

CONCLUSIONS

The _ab_ _initio_ calculations in this work have predicted that a bent rhodium carbonyl hydride species is much more stable than a rhodium formyl species and that there is no energy barrier which would prevent the formyl species from collapsing to the carbonyl hydride species which rationalizes the detection of the former, but not the latter, by infrared for supported Rh catalysts. The calculations also predict that the Rh-H stretching frequency for the rhodium carbonyl hydride species should occur some 300 - 400 cm^{-1} lower than the corresponding frequencies for rhodium organometallic complexes. Such a band may exist for Rh/TiO_2, but if it does, it unfortunately overlaps the hydrated support band, so we can not definitely conclude that the Rh-H stretch does not lie under the band for the C-O stretch for the rhodium carbonyl hydride species. The calculations do rationalize the ability of the hydride ligand to enhance C-O bond dissociation on supported rhodium.

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Table I. Absolute Energies (hartrees) of Various Species From Basis Set 1 (BAS1) and Basis Set 2 (BAS2) and Zero Point Energy (kcal/mol).

	Mol Sym	Elec Sym	BAS1			BAS2			ZPE / BAS1[a]
			HF	MP2	MP3	HF	MP2	MP3	
	H	K ^{2}S	-0.49328	-0.49328	-0.49328	-0.49328	-0.49328	-0.49328	0.0
	CO	C$_{\infty v}$ $^1\Sigma^+$	-112.66722	-112.87762	-112.86130	-112.67150	-112.88603	-112.86867	3.27(0)
	HCO	C$_s$ ^{2}A′	-113.18342	-113.38722	-113.38026	-113.18916	-113.39830	-113.38993	8.95(0)
	^{2}Rh	K ^{2}S	-22.01342	-22.01854	-22.02041				0.0
	^{4}Rh	K ^{4}F	-22.08945	-22.09266	-22.09387	-22.09158	-22.13680	-22.14022	0.0
	^{1}RhH	C$_{\infty v}$ $^1\Sigma^+$	-22.59504	-22.61754	-22.62594	-22.62783	-22.71588	-22.71912	2.14(0)
	^{3}RhH	C$_{\infty v}$ $^3\Delta$	-22.66187	-22.67823	-22.68352	-22.68331	-22.74722	-22.75250	1.62(0)
	^{2}RhCO[b]	C$_{\infty v}$ $^2\Delta$	-134.70140	-134.92574	-134.91612	-134.72052	-134.99011	-134.98109	
	^{4}RhCO	C$_{\infty v}$ $^4\Sigma$	-134.74498	-134.97051	-134.95847	-134.76670	-135.03800	-135.02640	
1	HRhCO	C$_{\infty v}$ $^1\Sigma^+$	-135.30433	-135.56281	-135.55129	-135.33950	-135.66845	-135.64454	9.02(0)
2	H‐RhCO	C$_s$ ^{1}A′	-135.30650	-135.59126	-135.57504	-135.34586	-135.71012	-135.67264	8.54(0)
3	O=RhCH	C$_s$ ^{1}A′	-135.28502	-135.53326	-135.53336	-135.32082	-135.64377	-135.63073	10.72(0)
4	TS	C$_s$ ^{1}A′	-135.27107	-135.56039	-135.54613	-135.30752	-135.68006	-135.64066	7.64(1)

a) Zero point energy and number of calculated negative frequencies in parentheses.

b) A highly spin contaminated wavefunction is obtained with BAS1 ($<S^2>$ expected, 0.75; found 1.76) and with BAS2 ($<S^2>$ expected, 0.75; found 1.76).

Table II. Relative Energies (kcal/mol) of Species on the HRhCO Potential Energy Surface

Comparison[a]	BAS1			BAS2			best
	HF	MP2	MP3	HF	MP2	MP3	
^{2}Rh – ^{4}Rh	47.7	46.5	46.1				46.1[b]
^{1}RhH – ^{3}RhH	41.9	38.1	36.1	34.8	19.7	21.0	21.5
^{2}RhCO – ^{4}RhCO	27.4	28.1	26.6	29.0	30.1	28.4	28.4[c]
1 HRhCO	1.4	17.8	14.9	4.0	26.2	17.6	18.1
2 H RhCO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3 RhCH (O)	13.5	36.4	26.2	15.7	41.6	26.3	28.5
4 TS	22.2	19.4	18.1	24.1	18.9	20.1	19.2
^{1}1 – ^{3}1	–55.3	–62.1	–65.7	–49.7	–49.4	–54.7	–54.7[d]
^{1}2 – ^{3}2	–56.7	–79.0	–71.3	–55.2	–91.8	–73.8	–73.8[d]
^{1}3 – ^{3}3	29.5	26.4	23.6	22.8	6.8	9.9	9.9[d]
^{1}4 – ^{3}4	0.1	–14.2	–11.5	–2.3	–28.9	–16.3	–16.3[d]

a) A comparison is made of the energy of the first state relative to the second state. Geometries on the singlet HRhCO potential energy surface (1-4) are relative to **2**. Singlet – triplet splittings of **1** – **4** are computed at the optimized singlet geometries. A positive value indicates that the higher multiplicity is more stable.

b) A contaminated spin state is obtained for the doublet state with BAS2. Best value is MP3/BAS1.

c) Zero point correction is not included. A contaminated state is obtained for the doublet state with BAS1 and BAS2.

d) Triplet energy is computed at the singlet geometry. Zero point correction is not included.

Table III. Computed Bond Energies (kcal/mol) at Several Levels of Theory

Bond	BAS1			BAS2			best[a]
	HF	MP2	MP3	HF	MP2	MP3	
^{3}Rh—H	49.7	57.9	60.5	61.8	73.5	74.7	73.1
^{4}Rh—CO	−7.3	0.1	2.1	2.3	9.5	11.0	11.0[b]
^{1}Rh—C(=O)H	7.6	33.5	37.2	25.2	68.2	63.1	61.3
^{1}H–RhCO	42.8	80.1	77.4	53.9	112.3	96.0	96.0[b]
^{1}H–Rh—CO	−14.2	22.2	19.0	−5.6	48.2	32.3	28.6

a) At the MP3/BAS2 + ZPC/BAS1 level of theory.

b) Best Level is MP3/BAS2. Zero point correction is not included.

Table IV. Vibrational Frequencies[a] (cm^{-1}), Deuterium Isotope Shifts (cm^{-1}), and Intensities (km/mol) at the BAS1 level

Molecule	Type	Sym	Freq(Shift)	Intensity	Exp
CO	C–O	σ	2034	146	2143[b]
HCO	H–C–O	a'	1098 (862)	42	1090 (852)[c]
	C–O	a'	1680 (1659)	81	1861 (1800)[c]
	C–H	a'	2793 (2026)	28	2488 (1937)[c]
^{1}RhH	Rh–H	σ	1333 (948)	695	
^{3}RhH	Rh–H	σ	1008 (717)	377	
HRhCO	Rh–C–O	π	234 (209)	160	
	Rh–C	σ	311 (310)	14	
	H–Rh–C	π	697 (561)	75	
	Rh–H	σ	1433 (1019)	2329	
	C–O	σ	2010 (2009)	644	
H RhCO	Rh–C–O	a'	282 (261)	17	
	out-of-plane	a"	327 (326)	2	
	Rh–C	a'	343 (338)	36	
	H–Rh–C	a'	753 (589)	100	
	Rh–H	a'	1643 (1169)	1184	
	C–O	a'	1971 (1968)	692	2037 (2032)[d]
O RhCH	Rh–C–O	a'	167 (165)	21	
	Rh–C	a'	352 (324)	2	
	out-of-plane	a"	674 (559)	17	
	Rh–C–H	a'	1319 (1015)	52	
	C–O	a'	1559 (1555)	268	
	C–H	a'	2604 (1905)	302	
TS	H–Rh–C	a'	577i[e]	488	
	Rh–C–O	a'	386	17	
	out-of-plane	a"	424	7	
	C–H	a'	811	232	
	Rh–H	a'	1331	419	
	C–O	a"	1805	534	

a) All frequencies have been scaled by 0.89 (see ref. 19); shift refers to the frequency for the analogous deuterated species.
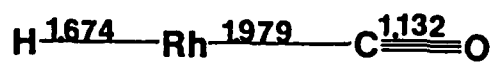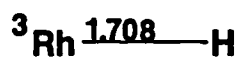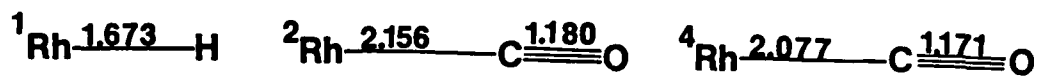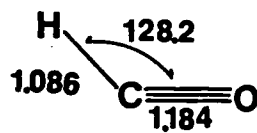b) Ref. 20.
c) Ref. 21.
d) This work.
e) Imaginary transition vector (negative eigenvalue of the force constant matrix).
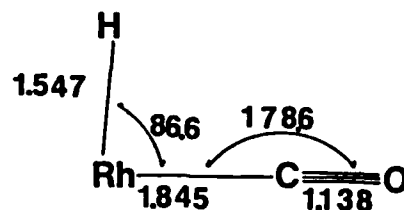
FIGURE CAPTIONS

Figure 1. Geometric parameters (bond lengths in Å, bond angles in degrees) for the species for which computations are reported in this work.

Figure 2. Infrared spectra of a 2.2% Rh/TiO_2 film (4.3 mg cm^{-2}) following reduction in H_2 at 480 K, evacuation for 1 h at 490 K, and evacuation to 10^{-6} Torr at 298 K overnight then (a) introduction of 77.4 torr of a 1:4 mixture of CO_2/H_2, heating at 440 K for 1 h, and evacuation to 10^{-3} torr at 298 K; (b) after contact with 100 torr D_2 at 298 K overnight.
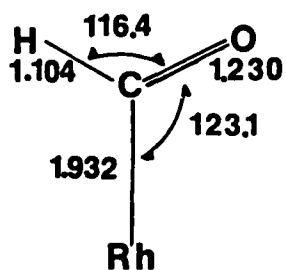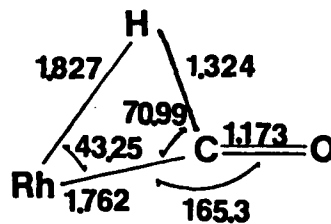
C≡O 1.131

H 128.2
1.086 C≡O
1.184

¹Rh—1.673—H   ²Rh—2.156—C≡O 1.180   ⁴Rh—2.077—C≡O 1.171

³Rh—1.708—H

H—1.674—Rh—1979—C≡O 1.132

1

H
1.547
Rh—1.845—C≡O
86.6 1786
1.138

2

H 116.4 O
1.104 C 1.230
1.932 123.1
Rh

3

H
1.827 1.324
70.99
43.25 C—1.173—O
Rh—1.762
165.3

4 (TS)

2.2% Rh/TiO₂
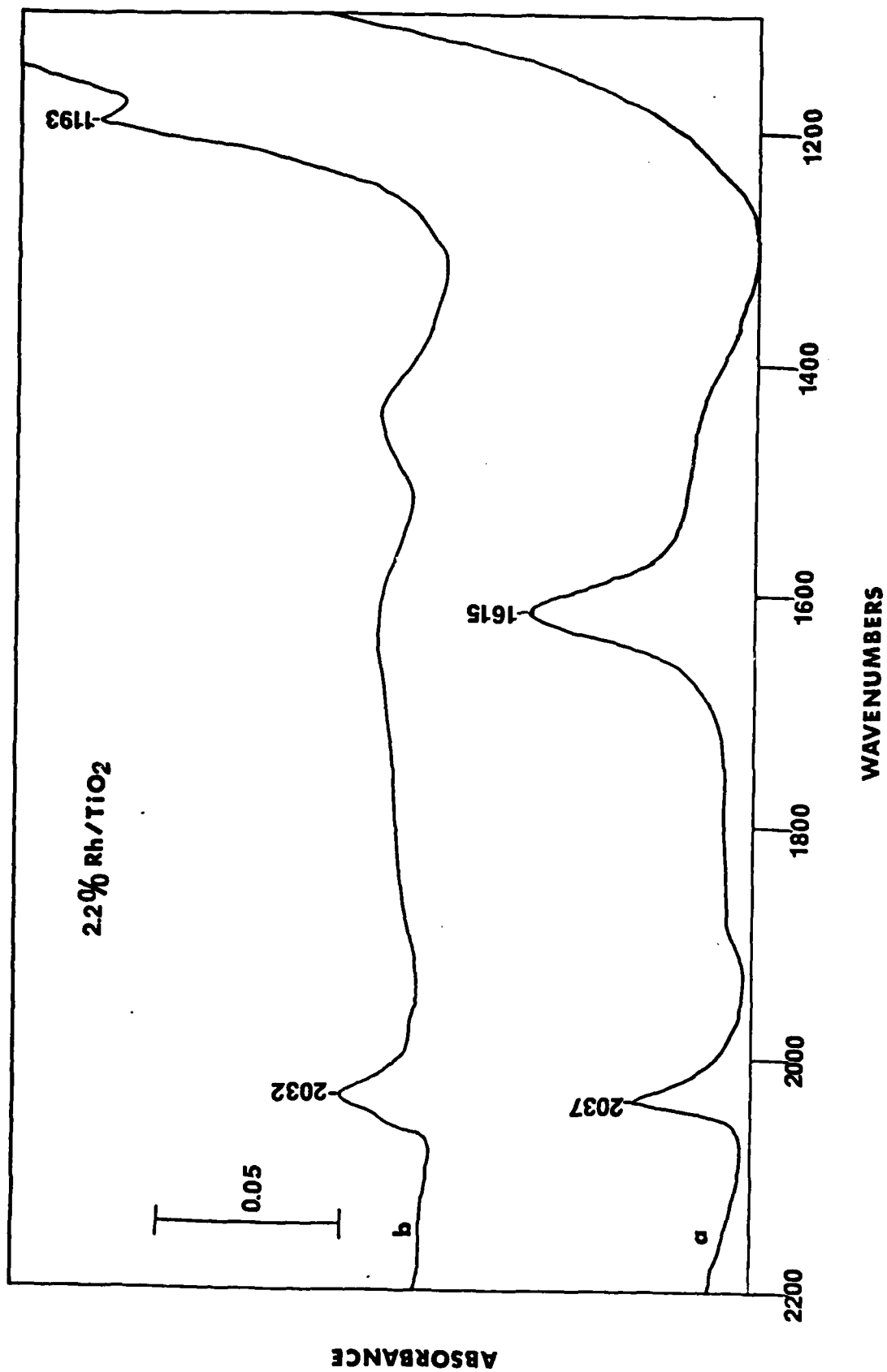
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